
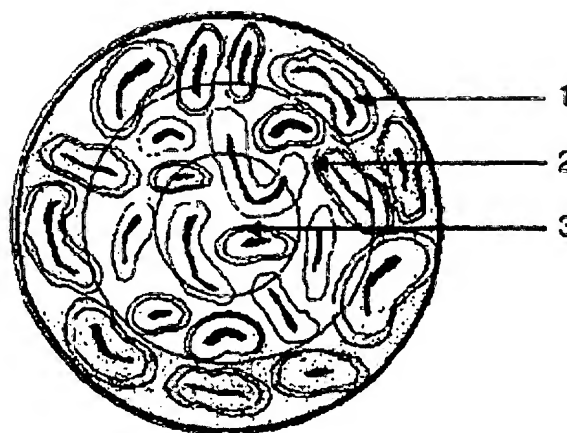


CHITOSAN-CONTAINING SPUN YARN AND METHOD FOR PRODUCING THE SAME**Patent number:** AU2002345412**Publication date:** 2003-07-15**Inventor:** KIM YOUNG-JUN; SON TAE-WON; KIM WON-KI**Applicant:** IBEKS TECHNOLOGIES CO LTD**Classification:****- international:** D02G3/00**- european:****Application number:** AU20020345412 20020703**Priority number(s):** WO2002KR01257 20020703; KR20010084172
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Disclosed is a chitosan gradated spun yarn in which chitosan-coated staple fibers decrease in relative concentration from outer to inner region on a cross section of the yarn. Consisting of 5-99 wt% of a chitosan-coated staple fiber and 1-95 wt% a non-coated staple fiber, the chitosan gradated spun yarn comprises chitosan in an amount of 1-5 wt% in an outer area on the cross section of the yarn, in an amount of 0.5-1 wt% in a middle area, and in an amount of 0.1-0.5 wt% in a central area. The yarn shows the same fiber properties as those of the spun yarn made of cellulose or proteins and can perform the functions of pure chitosan fibers in spite of its low content of chitosan. Also, the yarn is greatly improved not only in the adhesion between chitosan and fibrous components, but also in the durability of chitosan through a process including the pretreatment of the fiber, the aging of the chitosan solution, and post-coating fixation. Also provided is a method for producing such a chitosan gradated spun yarn.

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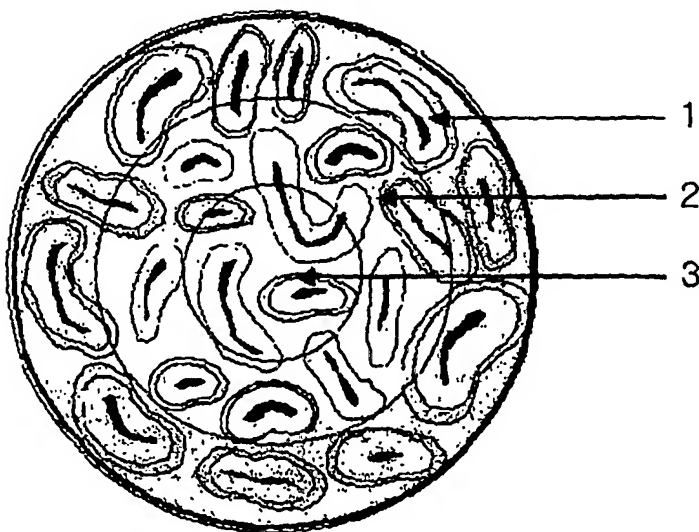
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- (71) Applicant (*for all designated States except US*): **IBEKS TECHNOLOGIES CO., LTD.** [KR/KR]; 646-2, Naebalsan-dong, Gangseo-gu, 157-280 Seoul (KR).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **KIM, Young-Jun** [US/US]; 727 S. Ardmore Avenue #801, Los Angeles, CA 90005 (US). **SON, Tae-Won** [KR/KR]; 101-1301 Hyundai Apt., 1072-3 Jisan 2-dong, Soosung-gu, 706-090 Daegu (KR). **KIM, Won-Ki** [KR/KR]; 1440-6 Pyoungri 4-dong, Seo-gu, 703-010 Daegu (KR).
- (74) Agent: **SON, Won**; C & S Patent and Law Office, C-2306 Daelim Acrotel, 467-6 Dogok-dong, Gangnam-ku, 135-270 Seoul (KR).
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(54) Title: **CHITOSAN-CONTAINING SPUN YARN AND METHOD FOR PRODUCING THE SAME**



(57) Abstract: Disclosed is a chitosan gradated spun yarn in which chitosan-coated staple fibers decrease in relative concentration from outer to inner region on a cross section of the yarn. Consisting of 5-99 wt% of a chitosan-coated staple fiber and 1-95 wt% a non-coated staple fiber, the chitosan gradated spun yarn comprises chitosan in an amount of 1-5 wt% in an outer area on the cross section of the yarn, in an amount of 0.5-1 wt% in a middle area, and in an amount of 0.1-0.5 wt% in a central area. The yarn shows the same fiber properties as those of the spun yarn made of cellulose or proteins and can perform the functions of pure chitosan fibers in spite of its low content of chitosan. Also, the yarn is greatly improved not only in the adhesion between chitosan and fibrous components, but also in the durability of chitosan through a process including the pretreatment of the fiber, the

aging of the chitosan solution, and post-coating fixation. Also provided is a method for producing such a chitosan gradated spun yarn.

CHITOSAN-CONTAINING SPUN YARN AND METHOD FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

5

1. Field of the invention

The present invention relates, in general, to a natural fiber containing chitosan and, more particularly, to a natural, spun yarn coated with chitosan in such a gradated structure as to have a lower density of chitosan-coated staples at a site nearer the core of the spun yarn. Also, the present invention is concerned with a method for producing such a spun yarn. Exhibiting biocompatible functions with maintenance of spun yarn properties, the chitosan-containing spun yarn can be used as a raw material not only for clothing with medical functions including antibacterial activity, hemostatic activity and tissue culture, but also for clothes, sheets and paper with antibacterial and deodorization activities.

20

2. Description of the Prior Art

The term "natural fibers" as used herein comprises cellulose fibers such as cotton and linen, regenerated fibers such as rayon and acetate, and protein fibers such as wool and silk, as well as regenerated protein fibers such as meat protein fibers and casein fibers.

Useful as a raw material for clothing, paper, wooden products, etc., cellulose such as cotton, linen and pulp, which naturally occur in plants, are closely related to human daily life and are expected to find new and continuing various applications in the future, as before.

30

Protein fibers from animals have been used by mankind for 5,000 years. Particularly, wools, silks, angora wools and cashmeres have been widely used in the human life. In the past, only natural protein fibers obtained from the nature, such as fur, feather, wool, etc., were used. In recent times, there has been increased a demand for protein fibers. To meet the demand, protein fibers are prepared from various sources including animal flesh, milk, grains and beans.

Chitin is quantitatively found in the shells of crustaceans, such as crabs and shrimps, and insects, and in the cell walls of fungi, mushrooms and bacteria, and along with potassium carbonate, proteins, lipids, and pigments, serves to support the main structure of the shells and exoskeletons of various animals. Despite its abundance in nature, chitin has not been effectively utilized because of its low solubility in aqueous solutions. Owing to this problem, chitin is difficult to form into fibers or films and thus, has found limited applications.

U.S. Pat. No. 3,533,940 discloses a method for preparing chitosan from chitin, along with its application to fibers and films. For possible applications, the prepared chitosan is dissolved in aqueous organic solutions.

U.S. Pat. No. 4,699,135 teaches that chitin can be dissolved in polar solvents such as lithium chloride-containing dimethyl acetyl amide to produce chitin fibers. Also, disclosed is the production of chitosan staples from a solution of chitosan in an aqueous acetic acid solution.

U.S. Pat. No. 5,897,821 offers a method for

manufacturing chitosan fiber wherein chitosan is dissolved in an aqueous solution of sodium thiocyanate and the resulting spinning solution is subjected to a wet spinning process to manufacture a chitosan fiber.

5 U.S. Pat. No. 5,900,479 describes the production of films and fibers of water-insoluble chitin using an aqueous organic acid solution of chitosan.

In addition to these, many other techniques for utilizing chitin or chitosan as raw materials in producing
10 films and fibers are disclosed. In addition, active research has been directed to the production of biocompatible, hygienic products of chitin or chitosan fibers suitable for use in clinical medicine fields and to their possible applications. As a result, various
15 relevant techniques are developed and disclosed at present.

Meanwhile, cellulose and chitosan, both a kind of polysaccharides, are very similar in structure, so that there is high physical and chemical compatibility therebetween. Taking advantage of these properties, a
20 complex is prepared from cellulose fibers and chitosan, or cotton fabrics are coated with chisotan to produce functional fabrics.

For example, Noguchi, et al. (Kobunshi Kagaku, 30, 320-326, 1973) produced a cellulose/chitin conjugate fiber
25 from cellulose xanthate and chitin xanthate in an alkali solution. Hasegawa et al. (J. Appl. Polym. Sci., vol. 45, 1837-1879, 1992) suggested the production of a cellulose/chitosan blended film from a solution of cellulose and chitosan in trifluoroacetic acid.

30 Hirano (Biotechnol. Ann. Rev., vol. 2, 237-258, 1996) disclosed chitin fibers, cellulose/chitin conjugate fibers,

manufacturing chitosan fiber wherein chitosan is dissolved in an aqueous solution of sodium thiocyanate and the resulting spinning solution is subjected to a wet spinning process to manufacture a chitosan fiber.

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and chitosan-coated synthetic fabrics, and their functionalities, including wettability, antibacterial and deodorization activities.

U.S. Pat. No. 5,114,788 discloses a fabric having
5 water absorption property and a method of manufacturing the fabric, in which a base fabric is immersed in or coated with a synthetic resin containing chitosan.

U.S. Pat. No. 5,306,550 discloses a biodegradable composite prepared from a mixture containing an aqueous
10 solution of an acid salt of chitosan, a thermoplastic resin, and cellulose fibers.

In addition, based on the physiological and hygienic functions of chitosan, many functional clothes, fabrics and fibers employ chitosan fibers, cellulose-chitosan
15 blend fibers, cellulose fiber-chitosan conjugate, and fabrics coated with chitosan-containing resins.

However, the conventional chitosan/cellulose conjugate fibers are reduced in their chitosan content and thus show poor chitosan functions with the lapse of time.

20 The patent application, entitled "Natural Fiber Coated with Chitosan and Method for Producing the Same", filed on the same date of this patent by the present inventors, discloses a fiber coated with a chitosan solution uniformly and firmly, but a spun yarn treated
25 with chitosan has not been disclosed.

Therefore, it is an object of the present invention to provide a chitosan-containing spun yarn which shows physiological and hygienic functions of chitosan,
30 with maintaining the desirable fiber properties.

It is another object of the present invention to

provide a method for producing such a chitosan-containing spun yarn.

SUMMARY OF THE INVENTION

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In accordance with an aspect of the present invention, there is provided a chitosan gradated spun yarn, comprising 5-99 % by weight of a chitosan-coated staple and 1-95 % by weight of a non-coated staple, in which
10 chitosan is present in an amount of 1-5 % by weight in the outer area of the cross section of the yarn, in an amount of 0.5-1 % by weight in the middle area, and in an amount of 0.1-0.5 % by weight in the central area, whereby the chitosan-coated staple is distributed in a decreasing
15 density gradient from the outer surface of the yarn to the center.

In accordance with another aspect of the present invention, there is provided a method for producing a chitosan gradated spun yarn, comprising the steps of:
20 pretreating a natural spun yarn in a solution at 0-90 °C for 1 min to 10 days, followed by dehydrating and conditioning the spun yarn at room temperature, so as to improve the affinity of the spun yarn for chitosan, said solution being selected from the group consisting of an
25 aqueous alkaline solution, an aqueous acidic solution, an aqueous salt solution, and mixtures thereof; preparing a chitosan solution by adding chitosan into a solvent, said solvent being selected from the group consisting of an aqueous acidic solution, an aqueous inorganic salt
30 solution, an organic solvent, and mixtures thereof, and aging the chitosan solution; applying the chitosan

solution to the pretreated natural yarn at 30-80 °C under a pressure of 1.5×10^5 - 5×10^5 N/m² for 1-10 hours, so as to coat or penetrate the chitosan solution onto the yarn; and stabilizing the chitosan-coated or penetrated spun yarn by thermal or alkali treatment.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a process flow diagram showing the production of a chitosan-coated spun yarn in accordance with an embodiment of the present invention.

Fig. 2 is a schematic cross-sectional view of the chitosan-coated spun yarn in accordance with the present invention.

Fig. 3 is a schematic cross-sectional view of a chitosan-coated spun yarn showing that the amount of chitosan is decreased from the outer surface to the center of the spun yarn.

Fig. 4 is an electron microphotograph showing the cross sections of the chitosan-coated spun yarns of the present invention.

Fig. 5 is an electron microphotograph showing the chitosan-coated spun yarns of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The chitosan-containing spun yarn of the present invention has a gradated structure in which the density of chitosan-coated fiber is reduced from the outer surface to the inner core of the yarn, whereby the spun yarn has different chitosan contents in cross-section and thus

shows chitosan functions semi-permanently with maintaining fiber properties.

Natural spun yarns suitable for use in the present invention are those that are prepared by spinning
5 cellulose fibers, prepared from seed, stem, and leaf fibers, such as cotton, linen, sisal, abacak, kapok, flax, jute, ramie, hemp, kenaf; protein fibers, including animal protein fibers such as wool, silk, cashmere, mohair, alpaca, and camel hair, meat protein fibers, casein fibers,
10 and vegetable protein fibers; and regenerated fibers such as viscose rayon, copper ammonium rayon, polynosic rayon, lyocell, tencel, cellulose acetate, and cellulose triacetate, alone or in combination.

Also, the spun yarns prepared from chitosan-coated
15 fiber may be used, alone or in combination with non-coated staples.

Preferred are those yarns that range from 5 to 100 μm in fineness and from 1 to 300 mm in length. In the case of cellulose fibers, their polymerization degrees are
20 preferably on the order of 100 to 20,000.

The spun yarn useful in the present invention may be provided using a conventional cotton spinning process comprising a series of blowing and opening, carding, combing, drawing, roving and spinning steps, or
25 conventional wool spinning process.

Chitosan suitable in the present invention ranges in polymerization degree from 20 to 10,000 and in deacetylation degree from 60 to 99.9 %. More preferable is chitosan which ranges in polymerization degree from 100
30 to 5,000 and in deacetylation degree from 85 to 99 %.

Chitosan is dissolved in an amount of 0.1 to 15 % by

weight in a solvent and preferably in an amount of 0.5 to 10 % by weight. Any solvent may be used if it is selected from aqueous acidic solutions, aqueous inorganic salt solutions and organic solvents.

5 To obtain an aqueous acidic solution useful in the present invention, water is added with 0.1 to 20 % by weight of an acid, examples of which include organic acids, such as acetic acid, lactic acid, formic acid, glycolic acid, acrylic acid, malic acid, propionic acid, succinic
10 acid, oxalic acid, ascorbic acid, gluconic acid, maleic acid, citric acid, glutamic acid, tartaric acid, toluene sulfonic acid, etc.; inorganic acids, such as hydrochloric acid, sulfuric acid, and phosphoric acid.

Available inorganic salt solutions contain an
15 inorganic salt at an amount of 10-70 wt% in water. Examples of useful inorganic salts include sodium thioisocyanate, zinc chloride, calcium chloride, sodium chloride, potassium chloride, and lithium chloride.

Useful organic solvents in the present invention are
20 polar, examples of which include dimethylacetamide, N-methylpyrrolidone, dimethylformamide, diethylacetamide, trifluoroacetic acid, trichloroacetic acid, methylene chloride, and tetrachloroethane. In order to obtain higher polarity, one or more selected from the above-
25 mentioned inorganic metal salts may be added at an amount of 1-10 wt% to the organic solvent.

With reference to Fig. 2, there is shown a spun yarn which has chitosan coated thereon and penetrated thereto. As seen in Fig. 2, the spun yarn is composed of staple
30 fibers having a sheath-core structure in which a core fiber 2 is surrounded by a chitosan sheath layer 1, and

staple fibers consisting only of core fiber 2.

With reference to Fig. 3, a more detailed structure of the spun yarn is shown in a cross sectional view. As seen, the chitosan-coated staples are mainly distributed
5 in the outer region a of the spun yarn while chitosan-coated staple fibers coexist with non-coated staple fibers in the middle region b. In contrast, non-coated staples are more abundant than chitosan-coated staples in the center region c of the spun yarn. The chitosan coated
10 over the staples becomes thinner as it goes from the outer region of the spun yarn to the inner region.

Thus, for example, when the spun yarn of the present invention is applied to the body, chitosan highly compatible with and beneficial to the body is focused in
15 the outer region while most of non-coated staples are distributed in the inner region, thereby allowing the spun yarn to maintain desirable fiber properties.

Being in firm contact with the staples, chitosan can maintain its function semi-permanently.

20 Depending on its purposes and kinds, the chitosan gradated spun yarn of the present invention is composed of 5-99 % by weight of chitosan-coated staples and 1-95 by % of non-coated staples.

Based on the total weight of the chitosan gradated
25 spun yarn of the present invention, the total staple fibers are present in an amount of 40 to 99 % by weight with the total chitosan amounting to 1 to 60 % by weight. Besides, the chitosan gradated spun yarn of the present invention may comprise moisture and other components in an
30 amount of 0.1 to 12 % by weight.

From a cross-sectional standpoint, the chitosan

gradated spun yarn of the present invention comprises chitosan in a decreasing amount from the outer surface to the center. In the spun yarn of the present invention, chitosan is distributed in an amount of 1-5 % by weight at
5 a part from the outer surface to a point one third of the radius, in an amount of 0.5-1 % by weight at a part to the next one third point, and in an amount of 0.1-0.5 % by weight to the next one third point, that is to the center.

The chitosan-coated staple of the present invention
10 is 5-10 μm in fineness and 1-300 mm in length.

Below, a description will be given of the production of the chitosan-coated natural fiber.

In conventional techniques, it is impossible to coat chitosan on the whole surface of a staple as well as a
15 spun yarn. Even though chitosan is partially coated on the surface of a staple or a spun yarn, a binder or a coupling agent is additionally used to increase the lifetime of the chitosan coating, thereby ensuring its attachment onto the fiber.

20 By contrast, the present invention can produce a chitosan gradated structure of spun yarns with a great improvement in the adhesion and uniform coating of chitosan to the fiber, without use of additional binders or coupling agents, through a series of processes
25 including the pretreatment of the fiber, the aging of the chitosan solution, and post-coating fixation.

In order to increase the affinity between spun yarns and chitosan, spun yarns are pre-treated. This is achieved by immersing spun yarns in an aqueous alkali
30 solution, an aqueous acidic solution, or an aqueous salt solution.

Useful in the present invention is an aqueous solution containing 1-40 % by weight of an alkali metal oxide, examples of which include sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium hydroxide, calcium oxide, barium hydroxide and barium oxide.

An aqueous acidic solution useful for the pretreatment of natural fibers is obtained by dissolving in water 0.1 to 20 % by weight of an organic acid which is exemplified by acetic acid, lactic acid, formic acid, glycolic acid, oxalic acid, succinic acid, propionic acid, acrylic acid, glycolic acid, tartaric acid, maleic acid, citric acid, and glutamic acid.

Available inorganic salt solutions contain an inorganic salt at an amount of 1-50 wt% in water. Examples of useful inorganic salts include organic metal salts, such as sodium acetate, sodium lactate, potassium acetate, potassium lactate, sodium glycolate, and potassium glycolate; alcohol metal salts such as sodium ethoxide; and inorganic metal salts such as sodium chloride, lithium chloride, calcium chloride, potassium chloride, zinc chloride, and sodium thiocyanate.

After being immersed in a suitable aqueous solution at 0-90 °C for 1 min to 10 days, the spun yarns are dehydrated and then conditioned at room temperature.

The pretreatment for improving the affinity of spun yarns for chitosan may be conducted once in an aqueous solution or twice or more in the same aqueous solution or different aqueous solutions.

With an improvement in affinity for and adhesion onto chitosan, the pretreated spun yarns allow chitosan to be coated uniformly over their surface as well as over the

surface of their staples.

In one embodiment of the present invention, as mentioned above, a chitosan solution uses as a solvent an aqueous acidic solution, an inorganic salt solution or an organic solvent. The chitosan solution contains chitosan in an amount of 0.1-15 % by weight and more preferably 0.5-10 % by weight.

To be improved in uniformity over and adhesion onto spun yarns as well as their staples, the chitosan dissolved in the solvent is preferably aged at 0-50 °C for 1 hour to 10 days.

Next, the chitosan solution is applied to the fiber treated for affinity. The application may resort to any technique known in the art, including immersion and spraying. Preferably, the pretreated fiber is immersed in a chitosan solution.

As for the coating of spun yarns with a chitosan solution by an immersion technique, this is achieved by immersing the fiber in a chitosan solution under such a compression condition to penetrate the chitosan solution into spun yarns, and removing excess chitosan solution. In spraying step, a chitosan solution is uniformly sprayed over the whole area of a fiber.

The immersing step is preferably carried out at 30-80 °C at a pressure of 1.5×10^5 - 5×10^5 N/m² for 1-10 hours.

To fix the chitosan solution onto the spun yarns, a stabilization treatment is performed. This can be achieved by treating the chitosan-coated fiber thermally or with an aqueous alkali solution.

The stabilization by heat treatment is based on the fact that the chitosan coated on fibers is solidified by

heating and thus prevented from separating from the fiber
duet to physical force or solvent solubilization.
Preferably, the fiber is treated thermally at 60-160 °C
for 1-100 min.

5 Based on neutralization with alkali, the
stabilization by alkali treatment prevents the chitosan
coated on the fiber from separating from the fiber owing
to re-dissolution by external acid. This stabilization is
performed by treating chitosan-coated fibers with an
10 alkali solution at 0-80 °C for 1 min to 1 day.

Useful in the present invention is an aqueous
solution containing 0.1-20 % by weight of an alkali metal
oxide, examples of which include sodium hydroxide, calcium
hydroxide, potassium hydroxide, lithium hydroxide, calcium
15 oxide, barium oxide and barium hydroxide.

To promote the stabilization by alkali treatment, an
alcohol may be added in an amount of 0.1 to 10 % by weight.
Examples of useful alcohols include methanol, ethanol,
propanol, butanol and phenol.

20 The alkali stabilization requires washing and drying
processes after the alkali treatment.

With the chitosan gradated structure in which natural
fibers such as cellulose fibers are distributed at the
central area and natural fibers firmly coated with
25 chitosan are focused at the outer area, the stabilized
spun yarn of the present invention exhibits fiber
properties and chitosan functions in concert. Thus, the
chitosan gradated spun yarn of the present invention is a
novel material in which natural fiber's biocompatibility
30 coexists with chitosan functionalities.

Exhibiting biocompatible functions with maintenance

of spun yarn properties, the chitosan-containing spun yarn of the present invention can be used as a raw material not only for clothing with medical functions including antibacterial activity, hemostatic activity and tissue culture, but also for clothes, sheets and paper with antibacterial and deodorization activities.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLE 1

15 Treatment of Cellulose Fiber for Affinity

1.34 kg of 30 cellulose yarns uniform in fineness was immersed in an aqueous 20 wt% sodium hydroxide solution to complete saturation, followed by compressing the yarns to remove excess sodium hydroxide solution. After being aged for 1 day at room temperature, the cellulose yarns were treated in an aqueous 3 wt% acetic acid solution at 20 °C for 3 hours and then dried.

25 Preparation of Chitosan Solution

0.5 kg of chitosan powder with a viscosity of 11.6 cps was dissolved in 9.5 kg of an aqueous 3 wt% lactic acid solution and the resulting solution was aged at 5-10 °C for 72 hours. This was added with 40 kg of water, and stirred completely to give 50 kg of a chitosan solution.

Production of Chitosan Gradated Cotton Yarn

1 kg of the pretreated cellulose cotton yarns was immersed in 10 liters of the chitosan solution and let to stand for 1 hour at 40 °C while being immersed. After the removal of excess chitosan solution, the cellulose cotton yarns were conditioned at room temperature for 3 hours. The conditioned, chitosan-coated cellulose cotton yarns were, in part, dried at 60 °C for 60 min by use of a dryer. They were stabilized by thermal treatment at 150 °C for 10 min in a hot-air dryer to give a chitosan gradated structure.

Using an electron microscope, the chitosan gradated cotton yarn was examined for surface and cross-section conditions, and the results are given in Figs. 4 and 5, respectively. As seen, the cotton yarns were coated with smaller amounts of chitosan nearer the center.

Also, Fig. 5 shows that the chitosan gradated spun yarn of the present invention has the same shape as general cotton yarns.

EXAMPLE 2

A chitosan gradated cotton yarn was prepared in the same manner as in Example 1, with the modification that, instead of the stabilization through thermal treatment in a hot-air dryer, the stabilization of the yarn was achieved by chemical treatment in which the partially dried yarn was immersed in 5 liters of an aqueous 5 wt% sodium hydroxide solution at 20 °C for 1 hour and washed with hot and cool water to neutrality.

An examination showed that staples distributed in outer areas were wholly and uniformly covered with chitosan and the density of the coated staples sheath layer was lowered at an area nearer the center of the spun
5 yarn.

EXAMPELS 3 TO 5

Treatment with Different Solutions for Affinity
10 Improvement

1 kg of cellulose yarns ranging from 10 to 30 μm in fineness and from 40 to 80 mm in length was completely soaked in an aqueous 20wt% sodium hydroxide solution,
15 followed by compressing the fibers to remove excess sodium hydroxide solution. After being aged for 1 day at room temperature, the cellulose yarns were washed with water and then coated with chitosan (Example 3).

1 kg of cellulose yarns ranging from 10 to 30 μm in
20 fineness and from 40 to 80 mm in length was treated in an aqueous 3 wt% acetic acid solution at 20 °C for 3 hours, dried and coated with chitosan (Example 4).

1 kg of cellulose yarns ranging from 10 to 30 μm in fineness and from 40 to 80 mm in length was treated with
25 the aqueous sodium hydroxide solution and then with the aqueous acetic acid solution, followed by coating with chitosan (Example 5).

For use in coating the yarns, a chitosan solution was prepared by dissolving chitosan having a viscosity of 11.6
30 cps and a deacetylation degree of 99 % to a concentration of 2 % by weight in an aqueous 1 wt% lactic acid solution.

This chitosan solution was coated on the pretreated cellulose fibers in the same manner as in Example 1, to give a chitosan gradated cotton yarn.

The chitosan gradated cotton yarns were examined for their coating states and the results are given in Table 1, below.

TABLE 1

Example No.	3	4	5
Treatment sol.	Aq. NaOH	Aq. Acetic Acid	Aq. NaOH & aq. Acetic acid
Coated area	Whole surface	whole surface	whole surface

10

EXAMPLES 6 TO 12

Coating with Different Concentrations of Chitosan Solutions

15

Chitosan solutions were prepared by dissolving chitosan having a viscosity of 11.6 cps and a deacetylation degree of 99 % to concentrations of 0.5, 1, 1.5, 2, 2.5, 3, and 3.5 % by weight in aqueous 0.3, 0.5, 0.8, 1, 1.3, 1.5, and 1.8 wt% lactic acid solutions, respectively. These chitosan solutions were coated on the pretreated cotton yarns in the same manner as in Example 1, to give chitosan-gradated cotton yarns.

Examination results showed that staples of the spun yarns have a sheath-core structure of uniform thickness, with the sheath layer adhering firmly to the core.

25

TABLE 2

Example No.	6	7	8	9	10	11	12
Conc. of chitosan Solution(wt%)	0.5	1	1.5	2	2.5	3	3.5
Thickness of Chitosan coated on outer fiber(μ m)	0.02-1	0.05-1	0.05-2	1-2	0.1-2	0.5-3	0.5-3

EXAMPLES 13 TO 20

5

Solidification with Different Concentrations of Sodium Hydroxide Solution

A chitosan solution was prepared by dissolving
 10 chitosan having a viscosity of 11.6 cps and a deacetylation degree of 99 % to a concentration of 1 % by weight in an aqueous 0.5 wt% lactic acid solution. This chitosan solution was coated on the pretreated cotton yarns in the same manner as in Example 1 to give chitosan
 15 gradated cotton yarns, followed by treating the yarns in aqueous 0.5, 1, 2, 3, 4, 5, 7.5 and 10 wt% alkali solutions at 20 °C for 1 hour. The yarns were washed with hot and cold water to neutrality to stabilize the chitosan sheaths. Final chitosan gradated cotton yarns were
 20 obtained after washing with water and drying at 60 °C for 3 hours.

The yarns were examined for the adhesion of chitosan to yarn the results are given in Table 3, below. Coat adhesion was determined after there were conducted tests
 25 for washing fastness (20 rounds) and friction fastness.

TABLE 3

Example No.	13	14	15	16	17	18	19	20
NaOH Conc. (wt%)	0.5	1	2	3	4	5	7.5	10
Adhesion	Excellent	Good	Good	Good	Good	Good	Excellent	Good

The chitosan gradated spun yarn of the present invention, consisting of chitosan-coated staples and non-coated staples, shows the same fiber properties as those of the spun yarn made of cellulose or proteins and can perform the functions of pure chitosan fibers in spite of its low content of chitosan. Additionally, the chitosan gradated spun yarn is greatly improved not only in the adhesion between chitosan and fibrous components such as cellulose and protein, but also in the durability of chitosan through a process including the pretreatment of the fiber, the aging of the chitosan solution, and post-coating fixation. Even though staples forming an outer part of the spun yarn are broken off, chitosan-coated staples existing at a predetermined ratio in an inner area can act in place of them, maintaining the functionality of chitosan semi-permanently.

The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A chitosan gradated spun yarn, comprising 5-99 %
by weight of a chitosan-coated staple fibers and 1-95 % by
5 weight of a non-coated staple fibers, in which chitosan is
present in an amount of 1-5 % by weight in the outer area
of the cross section of the yarn, in an amount of 0.5-1 %
by weight in the middle area, and in an amount of 0.1-
0.5 % by weight in the central area, whereby the chitosan-
10 coated staple is distributed in a decreasing density
gradient from the outer region of the yarn to the center
region.

2. The chitosan gradated spun yarn as set forth in
15 claim 1, wherein the staple fiber is a natural yarn
selected from the group consisting of a cellulose fiber, a
protein fiber, a regenerated fiber, and mixtures thereof,
said cellulose fiber being selected from the group
consisting of cotton, linen, wooden fiber, sisal, abaca,
20 kapok, flax, jute, ramie, hemp, and kenaf, said protein
fiber being selected from the group consisting of animal
protein fiber, a meat protein fiber, a casein fiber, a
vegetable protein fiber, and mixtures thereof, said animal
protein fiber being selected from among wool, silk,
25 cashmere, mohair, alpaca, and camel hair, said regenerated
fiber being selected from the group consisting of viscose
rayon, copper ammonium rayon, polynosic rayon, lyocell,
tencel, cellulose acetate, cellulose triacetate, and
mixtures thereof.

30

3. The chitosan gradated spun yarn as set forth in

claim 2, wherein the natural yarn is a cellulose fiber having a polymerization degree of 100 to 20,000, with a water content of 10 % by weight or less.

5 4. The chitosan gradated spun yarn as set forth in claim 1, comprising a staple component in an amount of 40-99 % by weight and a chitosan component in an amount of 1-60 % by weight based on the total weight of the chitin gradated spun yarn.

10

5. The chitosan gradated spun yarn as set forth in claim 1, wherein the chitosan ranges from 20 to 10,000 in polymerization degree and from 60 to 99.9 % in deacetylation degree.

15

6. The chitosan gradated spun yarn as set forth in claim 5, wherein the chitosan ranges from 100 to 5,000 in polymerization degree and from 85 to 99 % in deacetylation degree.

20

7. A method for producing a chitosan gradated spun yarn, comprising the steps of:

pretreating a natural spun yarn in a solution at 0-90 °C for 1 min to 10 days, followed by dehydrating and
25 conditioning the spun yarn at room temperature, so as to improve the affinity of the spun yarn for chitosan, said solution being selected from the group consisting of an aqueous alkaline solution, an aqueous acidic solution, an aqueous salt solution, and mixtures thereof;

30

preparing a chitosan solution by adding chitosan into solvent, said solvent being selected from the group

consisting of an aqueous acidic solution, an aqueous inorganic salt solution, an organic solvent, and mixtures thereof, and aging the chitosan solution;

applying the chitosan solution to the pretreated
5 natural yarn at 30-80 °C under a pressure of 1.5×10^5 - 5×10^5 N/m² for 1-10 hours, so as to coat or penetrate the chitosan solution onto the yarn; and

stabilizing the chitosan-coated or penetrated spun yarn by thermal or alkali treatment.

10

8. The method as set forth in claim 7, wherein the pretreatment step is carried out in an aqueous solution containing 1-40 % by weight of an alkali metal oxide, said metal oxide being selected from the group consisting of
15 sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium hydroxide, calcium oxide, barium hydroxide, barium oxide, and mixture thereof; in an aqueous acidic solution containing 0.1 to 20 % by weight of an organic acid, said organic acid being selected from the group consisting of
20 acetic acid, lactic acid, formic acid, glycolic acid, oxalic acid, succinic acid, propionic acid, acrylic acid, glycolic acid, tartaric acid, maleic acid, citric acid, glutamic acid, and mixtures thereof; or in an aqueous salt solution containing an organic salt, an alcohol metal salt
25 or an inorganic salt in an amount of 1-50 % by weight, said useful organic salt being selected from the group consisting of sodium acetate, sodium lactate, potassium acetate, potassium lactate, sodium glycolate, potassium glycolate, and mixtures thereof, said alcohol metal salt
30 being sodium ethoxide, said inorganic salt being selected from the group consisting of sodium chloride, lithium

chloride, calcium chloride, potassium chloride, zinc chloride, sodium thiocyanate, and mixtures thereof.

9. The method as set forth in claim 7, wherein the
5 chitosan solution is prepared by dissolving chitosan in an aqueous acidic solution containing 0.1-20 % by weight of an organic acid or an inorganic acid, said organic acid being selected from the group consisting of acetic acid, lactic acid, formic acid, glycolic acid, acrylic acid,
10 malic acid, propionic acid, succinic acid, oxalic acid, ascorbic acid, gluconic acid, maleic acid, citric acid, glutamic acid, tartaric acid, toluene sulfonic acid, and mixtures thereof, said inorganic acid being selected from the group consisting of hydrochloric acid, sulfuric acid,
15 and phosphoric acid; in an aqueous solution containing 10-70 % by weight of an inorganic salt, said inorganic salt being selected from the group consisting of sodium thioisocyanate, zinc chloride, calcium chloride, sodium chloride, potassium chloride, lithium chloride, and
20 mixtures thereof; or in an organic solvent selected from the group dimethylacetamide, N-methylpyrrolidone, dimethylformamide, diethylacetamide, trifluoroacetic acid, trichloroacetic acid, methylene chloride, tetrachloroethane, and mixtures thereof.

25

10. The method as set forth in claim 7, wherein the aging step is carried out at 0-50 °C for 1 hours to 10 days.

30 11. The method as set forth in claim 7, wherein the chitosan solution contains chitosan in an amount of 0.1-

15 % by weight.

12. The method as set forth in claim 11, wherein the chitosan solution contains chitosan in an amount of 0.5-
5 10 % by weight.

13. The method as set forth in claim 7, wherein the stabilization step is carried out by thermal treatment at 60-160 °C for 1-100 min.

10

14. The method as set forth in claim 7, wherein the stabilizing step is carried out using an alkaline solution at 0-80 °C for 1 min to 1 day.

15 15. The method as set forth in claim 14, wherein the alkaline solution is prepared by dissolving an alkali salt in an amount of 0.1-20 % by weight in water, said alkali salt being selected from the group consisting of sodium hydroxide, calcium hydroxide, potassium hydroxide, lithium
hydroxide, calcium hydroxide, potassium hydroxide, lithium
20 hydroxide, potassium oxide, barium oxide, barium hydroxide, and mixtures thereof.

16. The method as set forth in claim 14, wherein the alkaline solution is added with 0.1-10 % by weight of an
25 alcohol selected from the group consisting of methanol, ethanol, propanol, butanol, phenol, and mixtures thereof.

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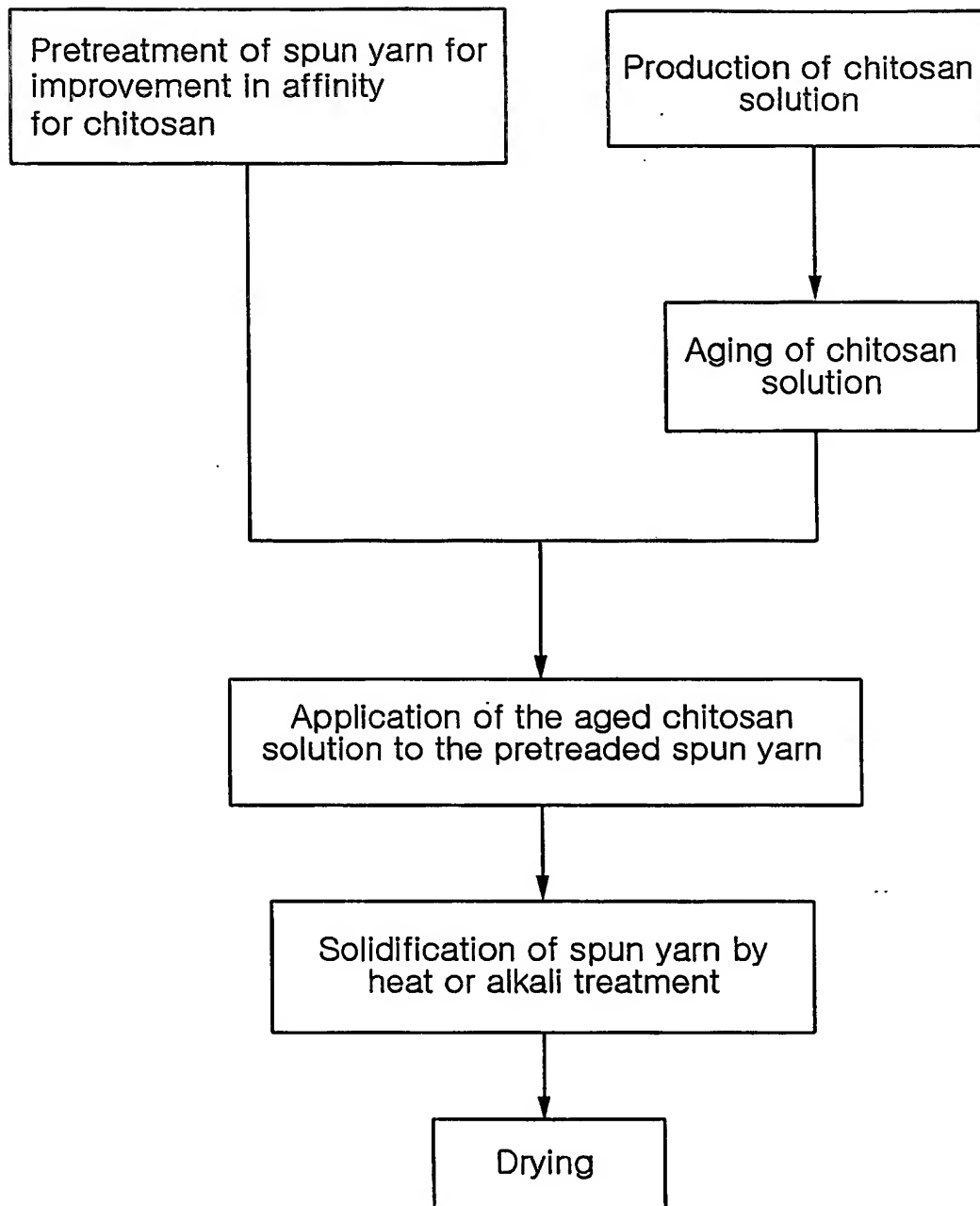


FIG. 1

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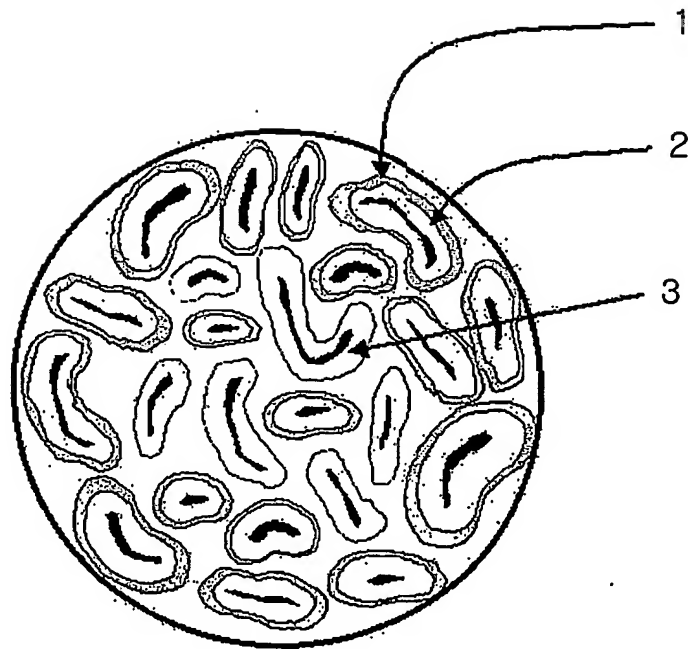


FIG. 2

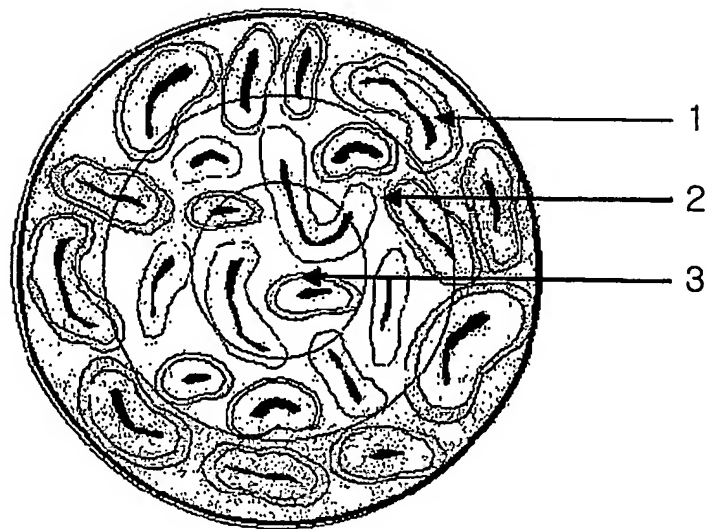


FIG. 3

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FIG. 4

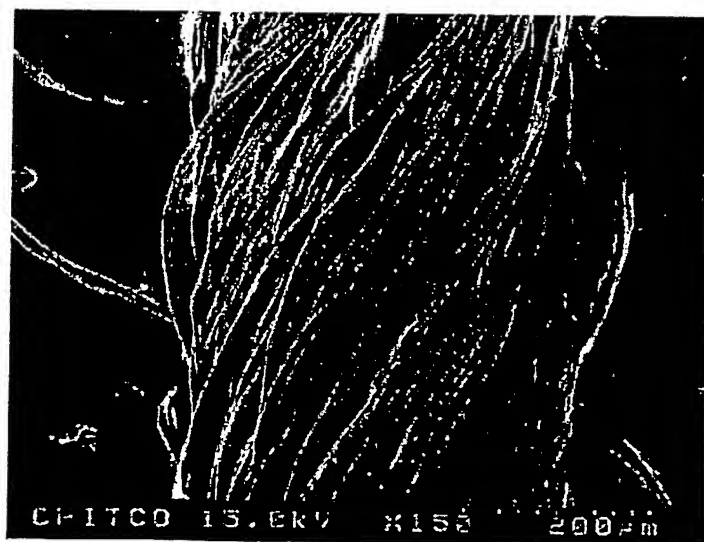


FIG. 5

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/KR 02/01257

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: D02G 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: D02G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2339717 A (MITSUBISHI) 9 February 2000 (09.02.00) <i>page 4, line 12 - page 5, line 16.</i>	1-16
A	EP 1162303 A1 (GUNZE) 12 December 2001 (12.12.01) <i>col. 3, line 55 - col. 5, line 20.</i>	1-16

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

4 October 2002 (04.10.2002)

Date of mailing of the international search report

23 October 2002 (23.10.2002)

Name and mailing address of the ISA/AT

Austrian Patent Office
Kohlmarkt 8-10; A-1014 Vienna

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Authorized officer

HUBER J.

Telephone No. 1/53424/313

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 02/01257-0

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